*Org. Geochem.* Vol. 11, No. 6, pp. 573–590, 1987
Printed in Great Britain. All rights reserved

0146-6380/87 $3.00 + 0.00
Copyright © 1987 Pergamon Journals Ltd

# Fractionated aromatic petroleums and the generation of gas-condensates

K. F. M. THOMPSON*
Atlantic Richfield Company, Exploration and Production Research Center, 2300 W. Plano Parkway, Plano, TX 75075, U.S.A.

(*Received* 5 *December* 1986; *accepted* 19 *May* 1987)

**Abstract**—Based on experimental and observational evidence, a mode of origin involving *evaporative fractionation* is proposed for a class of petroleums enriched in light aromatic and naphthenic hydrocarbons (benzene, toluene, meta-xylene, para-xylene, methylcyclopentane, cyclohexane, and methylcyclohexane). Progressive gas loss from gas-saturated oil is suggested as the causal mechanism, with simultaneous loss of light ends in gaseous solution, and accompanying fractionation. These processes were simulated experimentally.

Residual oils exhibit the following changes in their remaining light hydrocarbons, $<C_9$: (1) increase in aromaticity (in aromatic hydrocarbons relative to normal alkanes of similar molecular weight); (2) increase in "normality" (in unbranched alkanes and naphthenes relative to branched isomers), and (3) decrease in paraffinicity (in paraffins relative to naphthenes). Retrogressive changes in maturity indicators take place leading to spurious evidence of immaturity in residual oils and the derived evaporative condensates.

The phenomena occur in many basins, and are a key to understanding major aspects of petroleum variability. On the basis of aromaticity and paraffinicity relationships, evaporative gas-condensates are distinguishable from those generated by thermal cracking. Unfractionated thermal gas-condensates are rare. Evaporative condensates are the daughter products of oils which have suffered evaporative fractionation.

*Key words*: evaporative fractionation, molecular fractionation, petroleum alteration, petroleum fractionation, aromatic hydrocarbons, gasoline-range hydrocarbons, gas-condensates

## INTRODUCTION

### *Statement of problem*

An unusual class of petroleums was first encountered in U.S. Gulf Coast reservoirs of Tertiary age. These oils and condensates are distinguished by a deficiency of light ends, yet they possess abnormally high concentrations of low molecular weight aromatic hydrocarbons, particularly benzene, toluene, meta-xylene and para-xylene, as well as high concentrations of cycloalkanes, particularly methylcyclopentane, cyclohexane, and methylcyclohexane. A particularly informative instance was provided by a suite of oils reservoired adjacent to a salt dome. The oils were of diverse compositions in the gasoline range, but sufficiently similar in their heavy ends to indicate a common origin (Thompson, 1987). They exhibited varying degrees of light end loss. The losses appeared to be accompanied by fractionation in that the oils exhibited progressive changes in certain intermolecular ratios, the extent of which was proportional to the extent of light end loss. Four covariant series of compositional changes were recognized: (1) change of the dominant normal-alkane from $n$-$C_6$ to $n$-$C_{14}$; in the $C_5$ to $C_9$ range, (2) increase in aromaticity (in aromatic hydrocarbons relative to normal alkanes of similar molecular weight), (3) increase in "normality", (in unbranched alkanes and cycloalkanes relative to branched isomers), and (4) decrease in paraffinicity (paraffins relative to naphthenes). No such interrelated sequence of changes has been previously described.

Selected intermolecular ratios were compiled to describe the variation in the salt dome oils. The ratios were defined in a previously published study of the gasoline range hydrocarbons of oils (Thompson, 1983), as shown in Table 1.

### *Evaporative fractionation*

The term *evaporative fractionation* is suggested for the complex of phenomena involved in the separation of gas from oil in the subsurface. Fractionation can be defined by considering the initial development of a gas cap in an accumulation of gas-saturated oil. This could result from pressure reduction due to erosion or fault movement, or from the introduction of additional gas. Exsolution of gas involves the transfer of material of low and intermediate molecular weight into the vapor phase. All light petroleum components, having distributed themselves according to their vapor-liquid equilibrium constants, will occur in different proportions in vapor and liquid phases. The concentration ratio between any two will differ between vapor and liquid. These are the processes of molecular fractionation attendant upon phase separation.

*Present address: Department of Oceanography, Texas A&M University, College Station, TX 77843, U.S.A.

Table 1. Definitions and significances of gasoline compositional ratios

| Designation | Definition | Property Assessed |
|---|---|---|
| A | Benzene/n-Hexane | Aromaticity (fractionation) |
| B | Toluene/n-Heptane | Aromaticity (fractionation) |
| X | Xylene (m & p)/n-Octane | Aromaticity (fractionation) |
| C | (n-Hexane + n-Heptane)/ (Cyclohexane + Methylcyclohexane) | Paraffinicity (maturity) |
| I (Isoheptane Value) | (Methylhexanes (2- & 3-))/ (Dimethylcyclopentanes (1c3-, 1t3-, & 1t2-)) | Paraffinicity (maturity) |
| F | n-Heptane/Methylcyclohexane | Paraffinicity (maturity) |
| H (Heptane Value) | 100 * n-Heptane/ (Σ Cyclohexane through Methylcyclohexane*) | Paraffinicity (maturity) |
| R | n-Heptane/2-Methylhexane | Normality (branching) |
| U | Cyclohexane/Methylcyclopentane | Normality (branching) |

*excluding 1,cis-2-dimethylcyclopentane

The ability of a given compound to enter the vapor phase depends upon its vapor pressure, or more strictly, upon its fugacity. This is determined by molecular weight, isomeric structure, hydrocarbon class, and the composition of the mixture of hydrocarbons involved. The molecular weight effect is greatest among gases. The fugacities of methane and ethane greatly exceed that of propane, which exceeds that of the butanes. These compounds dominate the vapor phase. In the gasoline range there are numerous compounds of similar, or identical, molecular weight. Here the effects of structure and compound class predominate. Aromatic hydrocarbons behave extremely anomalously. Almost all except benzene are polar structures which induce polarity in other molecules and form transitory complexes of higher molecular weight, limiting their ability to escape from a liquid phase. Aromatic pi bond systems also lead to weak intermolecular attractions, evident in the relatively low vapor pressure of benzene.

The field of physical chemistry dealing with fractionation processes, and the distribution of material between coexisting liquids and gases, is that of fluid-phase equilibria. Reid *et al.* (1977) point out that the literature on phase equilibria has reached monumental proportions. It might therefore be expected that the relative amounts of any given compound in the vapor and liquid phases of a petroleum accumulation could be calculated from the extensive thermodynamic data available for pure compounds. This is not the case, although satisfactory approximations can be computed (Rowe, 1964). Exact quantification is not possible because the partial properties (those of the components of the mixture) are largely determined by the composition of the mixture, in addition to pressure and temperature. Petroleums are of almost infinitely variable composition.

*Vapor-liquid equilibria*

Prediction of equilibrium vapor compositions can be developed from the statement of thermodynamic equilibrium for every component, $i$, of the mixture in question:

$$f_i^{\mathrm{v}} = f_i^{\mathrm{L}} \tag{1}$$

where $f$ represents fugacity, v the vapor, and L the liquid phase. For component $i$, of mole fraction $y_i$ in the vapor phase:

$$f_i^{\mathrm{v}} = \phi_i y_i P \tag{2}$$

where $P$ is the pressure, and $\phi_i$ is the fugacity coefficient which depends upon temperature, pressure, and the mole fractions of all of the components of the vapor phase, not merely $y_i$. For ideal gases $\phi_i$ is unity.

In the liquid phase, containing mole fraction $x_i$ of component $i$:

$$f_i^{\mathrm{L}} = x_i f_i^0 \gamma_i \tag{3}$$

where $f_i^0$ is the standard fugacity of $i$ at the temperature of the system, and $\gamma_i$ is activity coefficient of

component $i$, dependent on temperature, pressure, and composition.

For ideal solutions, associated with vapor systems which are ideal gases, $\phi_i$ and $\gamma_i$ become unity, and equations (2) and (3) can be substituted in (1), giving

$$y_i P = x_i P_{vpi} \quad (4)$$

where $P_{vpi}$ represents the vapor pressure of component $i$ at system temperature. This is a statement of the combined laws of Raoult and Dalton. For applicability, mixtures must not only be ideal and at low pressure, but a temperature lower than the critical of the most volatile component. Methane dominates the mixtures of interest, but possesses a critical temperature of −82.1°C. Despite the limited applicability of (4), it indicates that the vapor pressures of pure hydrocarbons provide considerable insight into relative fugacities.

*Vapor-liquid equilibrium constants of petroleum systems*

Most techniques for the prediction of vapor-liquid compositional behaviour are based on empirical vapor-liquid equilibrium constants or ratios. Each "constant" is applicable only to a given component in a specific mixture, at a fixed temperature and pressure. The vapor-liquid equilibrium constant, $K$, is defined as follows:

$$K = y_i/x_i$$

at system pressure and temperature. Values of $K$ may be calculated through substitutions of the type shown in equations (2) and (3). Such are not pursued further here. The interested reader is referred to Reid *et al.* (1977) and references therein. A current review of computational models to assess the PVT behaviour of gas-condensate systems is provided by Stewart *et al.* (1984).

Two factors render the determination of $K$ values of complex methane-dominated hydrocarbon systems, those of interest in relation to evaporative fractionation, extremely difficult; firstly, the large number of components in petroleums, and secondly, their extraordinary variability in concentration. Published experimental studies are compiled by Daubert (1983) who reports over 100 systems. The majority are binary, and are evaluated at pressures and temperatures significantly lower than those encountered in petroleum reservoirs. The concept of convergence pressure has facilitated the estimation of $K$ values for the components of novel light petroleum mixtures from those of investigated mixtures of like convergence pressure. Such estimates rely on the occurrence of dominant methane and the similarity of components in the systems compared.

Improved simulations of the phase equilibria of gas-condensate and gas-oil systems can only be obtained by investigating complex, multicomponent systems. For example, Yarborough (1972) evaluated 43 methane-dominated mixtures of seven to ten components. Normal-alkanes through $n$-decane were represented, as well as minor amounts of nitrogen, carbon dioxide, hydrogen sulfide, and toluene, at pressures up to 4500 psia, and temperatures to 250°F. The equilibrium constant versus pressure relationships for seven components of a nine-component mixture at 100°F are shown in Fig. 1. The data are representative for a gas-condensate or associated gas.

There are no available vapor-liquid equilibrium constants for minor gasoline-range petroleum components in methane-dominated systems at reservoir temperatures and pressures. The work of Yarborough is of value in providing data relating to one minor component. He evaluated the effect of the addition of toluene to several of the systems investigated. The vapor-liquid equilibrium constants of the light and intermediate saturated hydrocarbons increased proportionately to the mole fraction of toluene added. Thus, aromatics facilitate the vaporization of saturated hydrocarbons, while they themselves accumulate in the residual liquid phase.

Yarborough (1972) provided details concerning a mixture (No. 6) comprising 0.8133 mole fraction methane; 0.0599 ethane; 0.0299 propane; 0.0346 $n$-pentane; 0.0252 $n$-heptane; 0.0189 toluene; and 0.0182 $n$-decane. At the pressures and temperatures

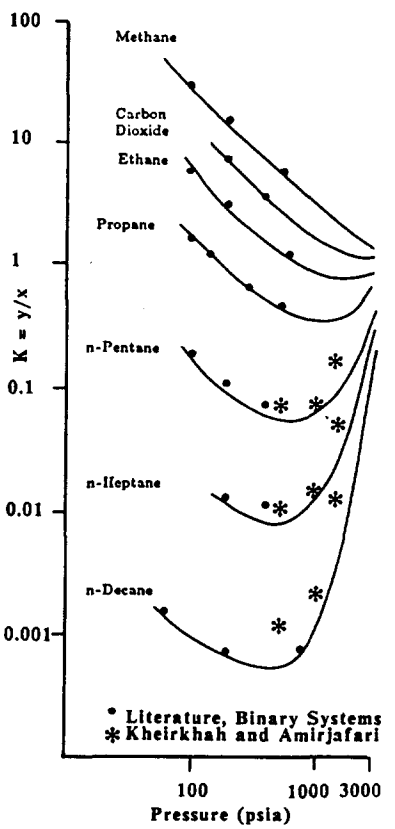


Fig. 1. Equilibrium constants of Yarborough, 1972 (solid lines) for selected compounds in a nine-component mixture at 100°F.

indicated below (Table 2), two phases occur; mole fractions of each component in vapor and liquid were published. For comparison with the data of the present study, mole fractions were recast as weight percentages, and the compositional ratio toluene/*n*-heptane (B, Table 1) was derived. The hypothetical single-phase value of B is 0.69. The data of Table 2 show that at elevated temperatures and pressures toluene is concentrated in the liquid (relatively high values of B), and *n*-heptane in the vapor. Furthermore, the aromaticity of the residual liquid is enhanced by increases in both pressure and temperature.

In addition to illustrating the behaviour of light aromatics in vaporization phenomena, equilibrium ratio data predict the behaviour of the normal-alkane envelope. The concept of evaporative fractionation involves contacting an oil (confined within a reservoir in nature, or within an experimental cylinder) with excess methane, and removing the equilibrated gas. Figure 2 illustrates the effect of ten such conceptual equilibration steps upon the oil represented by the normal-alkane profile A, employing actual equilibrium ratios in approximate calculations. The diagram is intended merely to illustrate the rapid, preferential removal of the lighter components, and the recession of the dominant alkane to progressively higher carbon numbers. These effects are due to the exponential decrease in the magnitude of equilibrium ratios with increasing carbon number. The later equilibrations illustrate the deltoid normal-alkane profile, or gas chromatographic envelope, considered to be characteristic of evaporative fractionation. This form is illustrated in later sections, both experimentally and in nature.

*Tertiary petroleum migration*

There are few published studies of tertiary petroleum migration (from reservoir to reservoir) describing accompanying modification of light end composition. Gussow (1954) postulated an important principle which he termed "differential entrapment". He suggested that a structurally ascending series of shelf anticlines is filled sequentially by migrating oil, and furthermore, that oil is eventually displaced by gas generated in the central basin region. Note that this would leave the deeper reservoirs filled with gas-condensate formed by evaporation of oil during displacement. Thompson (1980) found that these concepts provided elegant explanation of the compositional relationships observed in the San Juan Basin, New Mexico. Three basin margin oils were found to possess carbon isotope ratios averaging $-27.71 \pm 0.19$‰ PDB, while gas-condensate liquids in the mid-basin region averaged $-27.21 \pm 0.64$‰ PDB. The condensates are not isotopically heavier, as they would be if they represented thermal cracking residues. Likewise, paraffinicity ratios in the gasoline range which provide indices of thermal maturity (Thompson, 1979) were similar, although not identical, in oils and condensates. Heptane values averaged 20.51 and 19.76 in oils and condensates, respectively; isoheptane values were 1.24 and 1.80. The observed ranges of these two parameters in a large suite of North American oils (Thompson, 1983) were from 18 to 60 (heptane values) and 0.8–4.0 (isoheptane values) in normal and supermature oils, respectively. Thus the differences between oils and condensates observed in the San Juan Basin are relatively small.

Experimental studies of the solubility of petroleum and pure hydrocarbons in gas have been carried out principally by chemical and petroleum engineers. Such studies began with the pioneering work of W. N. Lacey (1930's), cited by Eilerts (1957, p. 194). Lacey's work was directed towards an understanding of gas-condensates and the question of whether or not liquid exists in the subsurface. Geochemical investigations into the actual sources of gas-condensates are few. It appears to be a present-day dogma of petroleum geochemistry that gas-con-

Table 2. Ratio toluene/*n*-heptane (B) in Yarborough's Mixture 6 at various pressures and temperatures

| Pressure MPa (psia) | TEMPERATURE °C (°F) 66 (150) | | 93 (200) | | 121 (250) | |
|---|---|---|---|---|---|---|
| | $B_{liq.}$ | $B_{vap.}$ | $B_{liq.}$ | $B_{vap.}$ | $B_{liq.}$ | $B_{vap.}$ |
| 7.14 (1035) | -- | -- | 0.76 | 0.56 | 0.78 | 0.61 |
| 10.67 (1547) | 0.75 | 0.55 | 0.76 | 0.60 | 0.79 | 0.62 |
| 14.10 (2045) | 0.75 | 0.60 | 0.76 | 0.63 | 0.79 | 0.66 |
| 17.46 (2532) | 0.77 | 0.62 | 0.79 | 0.63 | 0.80 | 0.66 |
| 20.88 (3029) | 0.78 | 0.65 | 0.79 | 0.66 | -- | -- |

B = toluene/n-heptane by wt.

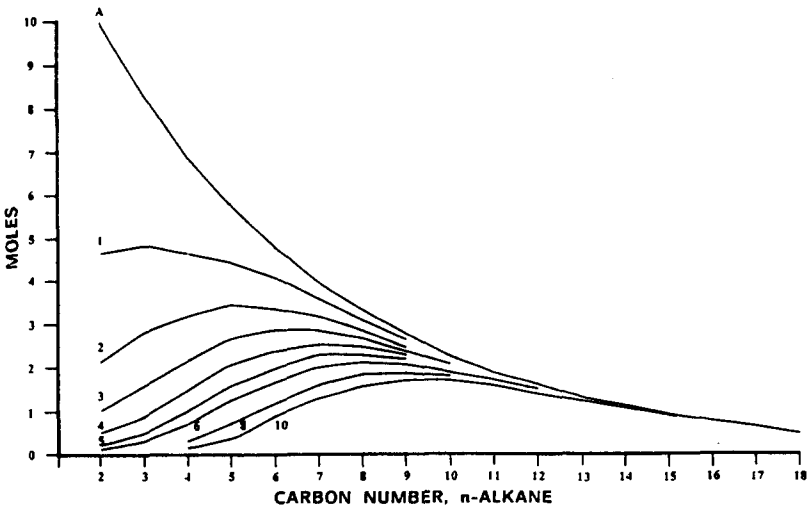


Fig. 2. Simulated behavior of normal-alkane mixture, initially of composition (A), after ten equilibrations with methane, each followed by removal of the gas phase.

densates are almost entirely the result of thermal cracking of oil during late catagenesis (equivalent vitrinite reflectance levels greater than 1.0–1.2%). Statements of this nature occur in all summary treatments. However, evidence will be presented indicating that numerous condensate liquids do not reflect extensive cracking, are of maturity levels normal for oils, and that they contain allochthonous methane. Such are termed here *evaporative condensates*; those due to late catagenesis are termed *thermal condensates*. Snowdon (1978), Connan and Cassou (1980), Rogers (1980), Snowdon and Powell (1982) and Nissenbaum *et al.* (1985) have claimed the existence of immature condensates, generated at reflectance levels below 0.6%. Such are discussed further in a subsequent section.

Zhuze and Yushkevich (1959) and Zhuze *et al.* (1962, 1963) determined the solubility of crude oils in gases at various pressures and temperatures, and determined hydrocarbon group compositions in distillation fractions. They employed the data to construct paraffin, naphthene, and aromatic profiles of oils and condensates, plotting concentrations versus average boiling point. They evaluated the mode of origin of certain gas-condensate accumulations, concluding in several cases that they represented oil fractions which had migrated in the vapor phase. Zhuze *et al.* observed and demonstrated experimentally that condensates originating in this fashion are enriched in paraffins, and depleted in aromatics. Price *et al.* (1983) investigated oil solubility in methane, particularly the solubility of heavy ends, for the purpose of defining migration mechanisms.

It appears that Zhuze *et al.* (*supra cit.*) were the first to describe the generation of gas-condensates by the segregation of gas and light ends from oil, without attendant thermal cracking, though this concept is implicit in the writings of Gussow (1954). They were also the first to observe the enrichment of light aromatic hydrocarbons in residual oils, an observation independently repeated in the course of the present study.

Silverman (1965) described the close association of light and heavy oils in a faulted multi-pay field, the Chevron Field, Kleberg County, south Texas. In explanation, he proposed "chemical differentiation" as the mechanism relating the various oil gravities, and a process of "separation migration" to account for it. He postulated that the gas cap of the deeper pools tended to bleed-off along faults, leaving residual oils (40° API), depleted in light ends, in deeper reservoirs. The postulate also suggested that light oils (59° API) were created in shallower reservoirs by retrograde condensation of the cap gas. His principal emphasis was a demonstration of the genetic relationship between lighter and heavier oils. For this purpose he quoted several light hydrocarbon compositional ratios. He did not employ the term "fractionation", nor did he investigate any related concept.

Hunt (1979, p. 215) suggested that migrating gas might segregate aromatics from oil, resulting in aromatic condensates, such as those of the Gulf Coast Pleistocene.

The present work differs from, and extends, that of Zhuze *et al.* and Silverman in the area of fractionation effects. Here such effects are expressed in terms of selected intermolecular ratios in the gasoline range, ratios which have been reported previously for large numbers of sedimentary rock extracts and oils (Thompson, 1979, 1983). Experimental studies led to criteria which, it is believed, assess the frequency of occurrence or severity of evaporative fractionation in terms of gas chromatographic data and, with certain

limitations, in terms of distillation—physical property data obtained by U.S. Bureau of Mines Routine Distillation Analyses (Thompson, 1987).

## EXPERIMENTAL

There are no available vapor-liquid equilibrium constants for minor gasoline-range petroleum components in methane-dominated systems, at reservoir pressures and temperatures. Therefore, no theoretical test can be made of the hypothesis that fractionation due to gas loss in the reservoir is responsible for variations in light end composition in the salt dome oils described above. When the oils were first analyzed it was necessary to consider the possibility that accidental loss of light ends might have taken place, either in the stock tank or in storage. The effects of vapor phase loss at elevated pressure and temperature were therefore investigated by experimentally modifying a series of oil samples. The resulting residual oils and condensates were analyzed by gas chromatography and the conventional suite of light hydrocarbon compositional ratios (Table 1) determined.

Experiments were carried out using standard engineering apparatus intended for phase equilibrium studies of petroleum fluids. The equipment principally comprised high pressure mercury pumps (Ruska, Inc.) and a steel pressure vessel capable of being maintained at constant, elevated temperature. Small volumes of oil were displaced into a mercury-sealed high-pressure cell (Ruska single-window), followed by sufficient methane to oversaturate the oil at the chosen final pressure and temperature. Details are given in Table 3. The cell was equilibrated for 48 hr with agitation (rocking), after which the vapor phase was bled-off under equilibrium pressure, maintained by pumping. The retrograde condensate from the vapor was precipitated in a condenser cooled by solid carbon dioxide. In Experiment 1, oil was equilibrated only once with methane. In Experimental Series 2 the residual oil left in the pressure vessel after an initial equilibration and removal of the vapor was equilibrated again with a further volume of methane. Thus, two condensates were obtained. In Experimental Series 3 the initial oil and subsequent residues were equilibrated eleven times with additional volumes of methane. Samples of the eleven condensates were obtained, but none of the residual oils. Methane alone was added to the cylinder, and only vapor was withdrawn.

Further information is available concerning the Series 2 fluids. Upon attaining the first contact equilibrium at 6000 psi and 260°F, the volumetric ratio of gas to oil in the cell was 0.632 l/l. Dissolution of methane in the oil expanded the latter by a volumetric factor of 1.07. After attaining the second contact equilibrium the ratio of gas to oil in the cell rose to 1.20, evidencing substantial loss of light ends from the oil when gas was bled-off after the first equilibration. The residual oil left in the cell at 6000 psig and 260°F after the second removal of gas was flashed to 0 psig and 69°F. Shrinkage by a factor of 0.711 occurred (formation volume factor of 1/0.711 or 1.407); the gas liberated from solution represented a gas/oil ratio of 859 scf/bbl.

Comparative experiments (Series 4) involving evaporation at room temperature were also carried out. A thin layer of the oil employed in Experiment 1 was allowed to stand in an open petri dish and was periodically sampled for analysis.

## RESULTS

In Experiment 1 stock tank oil from Sulfur Bluffs field, Hopkins County, east Texas (Paluxy Formation, 4500 feet) was employed, a high-sulfur oil of 24° API gravity. The oil is rich in light ends, having a nonane/nonadecane ratio of 6.72, compared to an average oil value of 2.5 (writer's unpublished data). The paraffinicity is high, having a heptane value of 37.5, and the oil is therefore supermature. Aromaticity is low. After treatment the oil was depleted in light ends, as in the illustrated examples of Experimental Series 2, shown in Fig. 3. The API gravity of the residual oil was 21°, and that of the derived condensate 46°. Compositional changes are indicated in Table 4. The residual oil is enhanced in aromaticity

Table 3. Conditions of experimental evaporative fractionation

| Experimental Series | No. of Steps | Volume (liters, N.P.T.) Oil | Gas | G.O.R. (cu. ft./bbl) | Equilibrium Conditions P, MPa (psi) | T, °C(°F) |
|---|---|---|---|---|---|---|
| 1 | 1 | 0.1 | 65 | 3652 | 41.4 (6000) | 126 (260) |
| 2 | 2 | 0.15 | 35 | 1309 | 44.8 (6500) | 126 (260) |
| 3 | 11 | 0.3 | 50 | 938 | 31.0 (4500) | 90 (194) |
| 4 | 2 | 0.01 | -- | -- | ambient | ambient |

Oil employed in Series 1 and 4 was from Sulfur Bluffs field, Lower Cretaceous, Texas; Series 2, Hartzog Draw field, Upper Cretaceous, Wyoming; Series 3, unidentified.

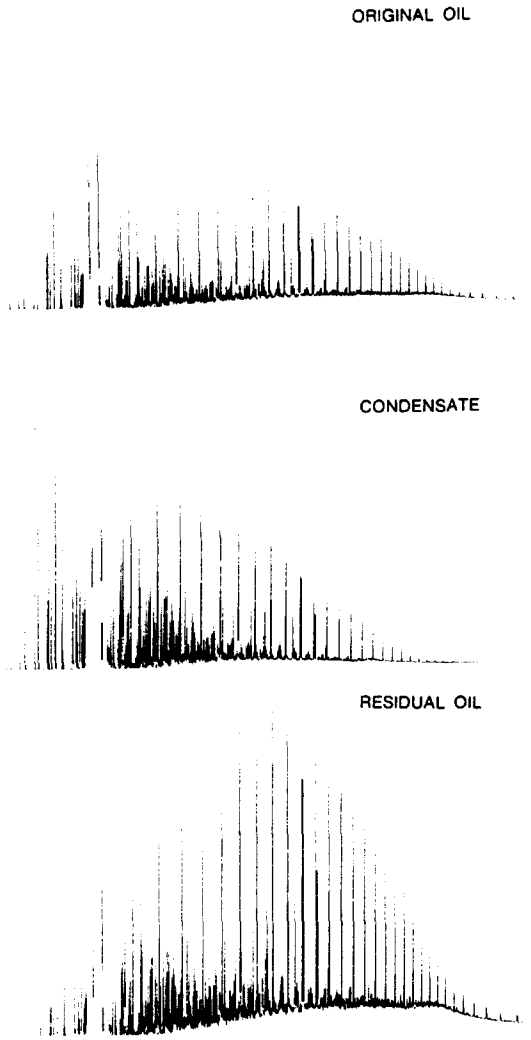


Fig. 3. Gas chromatograms of liquids from Experimental Series 2. Condensate is first-stage; residual oil is that after second stage. Subsequent condensates would have resembled the residual oil (compare Series 3).

and diminished in paraffinicity. The dominant alkane changed from $n$-$C_7$ to $n$-$C_{14}$. Thus the principal features of the salt dome oils were reproduced.

In collecting the condensate produced in Experiment 1, insufficient cooling was applied during removal of gas from the high pressure cylinder, allowing the escape of a smoke-like hydrocarbon vapor. Analysis of the condensed liquid showed substantial light end losses (line 3, Table 4). The losses invalidate any conclusions which might have been drawn from the aromaticity and paraffinicity ratios of the condensate of Experiment 1. The residual oil data are unimpaired.

Experimental Series 2 employed an oil of normal maturity (heptane value 21.2) and of intermediate aromaticity in terms of toluene and xylene. The oil is from Hartzog Draw field, Campbell County, Wyoming, produced from the Shannon Formation at 9485 ft. Initial API gravity was 35°. A single sample of oil was equilibrated twice with methane under pressure. The second residual oil was sampled, as well as both condensates, without evaporation loss. The first residual oil could not be sampled. The condenser was cooled with solid carbon dioxide. Changes in gasoline composition are detailed in Table 4. Once again the residual oil is enhanced in aromaticity and normality, but diminished in paraffinicity; the first condensate shows the converse effects. It is noteworthy that the second condensate increases in aromaticity, and decreases in paraffinicity, over the first. It may be inferred that if further steps were carried out, both the later condensates and the residual oils with which they were in equilibrium would become more aromatic than the initial oil. This trend was documented in Experimental Series 3.

Experimental Series 3 involved eleven methane equilibration steps employing a single sample of oil of undisclosed origin. The oil was of normal heptane value (21.3), but of intermediate aromaticity (B, 1.24; X, 0.81). After each equilibration the vapor phase was collected at liquid nitrogen temperature, distilled to a $C_{6+}$ liquid, then analyzed by gas chromatography. Resolution was lower than customary, so that several ratios could not be computed.

The first condensate is less aromatic and more paraffinic than the parent oil, as in Experiment 2. The second condensate shows similar but smaller differences, but the third and subsequent stages are more aromatic and less paraffinic than the initial oil, reversing the initial trend. In Series 3, the aromaticity of the condensates increases exponentially. It is important to bear in mind that such condensate was associated in the high pressure cylinder with a residual oil of slightly higher aromaticity, and lower paraffinicity, although the oils were not sampled. The condensates therefore mirror the generation of a series of light-end-depleted, aromatic, naphthenic oils which, it will be shown, have analogs of commonplace natural occurrence.

The condensate data of Series 3, combined with reliable inference concerning the unsampled residual oils, leads to the apparent anomaly of both parent and daughter phases changing in the same direction (increasing aromaticity) simultaneously. This is indeed the case, but had intermediate samples of oil been collected, it would have been found, for the $C_5$–$C_9$ range, that the $n$th residual oil was more aromatic, and the $n$th condensate less aromatic, then the ($n$-1)th residual oil.

Figure 4 is a representation of gas chromatographic data for the key low molecular weight compounds and normal-alkanes of the condensates of stages 1, 3, 7, and 11. Stage 1 (condensate 1) shows the usual exponential decrease in normal-alkanes expected in an unaltered oil, or in its initial vaporization product. With progressive fractionation (Step 3), the distribution becomes almost flat topped in the

Table 4. Analytical parameters, experimental oils and condensates

| Experiment | Sample | Aromaticity | | | Paraffinicity | | | | Normality | | Wt. %, Selected Alkanes | | | | | | | Ratios | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | A | B | X | C | I | F | H | U | R | $n\text{-}C_5$ | $n\text{-}C_6$ | $n\text{-}C_7$ | $n\text{-}C_8$ | $n\text{-}C_9$ | $n\text{-}C_{19}$ | $n\text{-}C_{29}$ | $n\text{-}C_9/n\text{-}C_{19}$ | Pr/Ph |
| 1 | Original Oil | 0.04 | 0.03 | 0.10 | 3.93 | 5.82 | 2.76 | 38.0 | 1.49 | 2.30 | 1.70 | 2.61 | 2.97 | 2.83 | 2.79 | 1.21 | 0.24 | 2.89 | 0.59 |
| 1 | Residual Oil | 0.07 | 0.04 | 0.13 | 1.62 | 4.86 | 2.19 | 39.7 | 1.89 | 2.91 | 0.18 | 0.63 | 1.29 | 1.78 | 2.17 | 1.74 | 0.32 | 1.58 | 0.58 |
| 1 | Condensate ++ | 0.04 | 0.03 | 0.14 | 3.10 | 5.60 | 2.92 | 46.0 | 2.25 | 3.42 | 0.03 | 0.21 | 1.00 | 2.31 | 3.70 | 1.53 | 0.14 | 3.07 | 0.57 |
| 2 | Original Oil | 0.04 | 0.22 | 0.27 | 1.09 | 0.98 | 0.77 | 21.2 | 0.71 | 2.15 | 1.60 | 1.74 | 1.87 | 1.88 | 1.76 | 1.13 | 0.25 | 1.56 | 1.78 |
| 2 | Residual Oil | 0.06 | 0.30 | 0.33 | 0.81 | 0.85 | 0.66 | 20.2 | 0.82 | 2.36 | 0.23 | 0.59 | 1.05 | 1.38 | 1.50 | 1.56 | 0.41 | 0.96 | 1.69 |
| 2 | Condensate 1 | 0.03 | 0.17 | 0.19 | 1.32 | 1.09 | 0.94 | 23.2 | 0.67 | 2.13 | 1.62 | 3.12 | 3.33 | 1.90 | 1.79 | 0.48 | 0.04 | 3.73 | 1.96 |
| 2 | Condensate 2 | 0.03 | 0.19 | 0.21 | 1.17 | 1.05 | 0.89 | 23.2 | 0.72 | 2.24 | 1.58 | 2.52 | 3.13 | 3.14 | 2.79 | 0.47 | 0.03 | 5.93 | 1.84 |
| 3 | Original Oil | 0.55 | 1.24 | 0.81 | 0.85 | 1.03 | 0.67 | 21.3 | 1.18 | 3.58 | - | - | - | - | - | - | | | |
| 3 | Condensate 1 + | * | 0.85 | 0.80 | * | * | 0.77 | 22.2 | * | * | 0.26+ | 10.32 | 3.69 | 3.46 | 3.09 | 0.03 | - | 103.0 | 2.25 |
| 3 | Condensate 2 + | * | 1.14 | 0.89 | * | * | 0.69 | 20.8 | * | * | 1.08 | 6.25 | 2.93 | 3.33 | 3.28 | 0.06 | - | 54.7 | 2.10 |
| 3 | Condensate 3 + | * | 1.33 | 1.05 | * | * | 0.62 | 20.3 | * | * | 0.38 | 3.27 | 2.22 | 3.08 | 3.69 | 0.04 | - | 92.3 | 2.37 |
| 3 | Condensate 4 + | * | 1.77 | 1.21 | * | * | 0.46 | 17.6 | * | * | 0.67 | 1.85 | 1.35 | 2.37 | 3.10 | 0.08 | - | 38.8 | 2.22 |
| 3 | Condensate 5 + | * | 2.24 | 1.40 | * | * | 0.45 | 17.9 | * | * | 0.08 | 0.73 | 0.83 | 1.84 | 2.69 | 0.10 | - | 26.9 | 2.28 |
| 3 | Condensate 6 + | * | 3.18 | 1.79 | * | * | 0.35 | 15.1 | * | * | 0.07 | 0.30 | 0.45 | 1.22 | 2.14 | 0.13 | - | 15.5 | 2.35 |
| 3 | Condensate 7 + | * | 4.50 | 2.25 | * | * | 0.29 | 13.2 | * | * | 0.05 | 0.14 | 0.26 | 0.85 | 1.69 | 0.18 | - | 9.4 | 2.21 |
| 3 | Condensate 8 + | * | 6.13 | 2.70 | * | * | 0.25 | 11.9 | * | * | 0.01 | 0.06 | 0.16 | 0.64 | 1.35 | 0.18 | - | 7.5 | 2.21 |
| 3 | Condensate 9 + | * | 8.00 | 3.72 | * | * | 0.20 | 10.7 | * | * | 0.02 | 0.03 | 0.08 | 0.36 | 1.09 | 0.22 | - | 5.0 | 2.17 |
| 3 | Condensate 10 + | * | 8.50 | 4.63 | * | * | 0.21 | 10.3 | * | * | 0.03 | 0.02 | 0.06 | 0.24 | 0.80 | 0.11 | - | 7.3 | 1.82 |
| 3 | Condensate 11 + | * | 7.00 | 10.14 | * | * | 0.20 | 10.0 | * | * | 0.05 | 0.00 | 0.01 | 0.07 | 0.51 | 0.32 | - | 1.6 | 2.14 |
| 4 | Oil, Evap. 0 min | 0.04 | 0.03 | 0.05 | 3.76 | 8.34 | 2.71 | 38.8 | 1.49 | 1.80 | 1.30 | 2.08 | 2.46 | 2.43 | 2.32 | 0.97 | 0.33 | 2.40 | 0.66 |
| 4 | Oil, Evap. 20 min | 0.23 | 0.03 | 0.06 | 3.28 | 7.65 | 2.41 | 41.9 | 0.40 | 2.12 | 0.21 | 0.62 | 1.44 | 2.18 | 2.46 | 1.06 | 0.38 | 2.32 | 0.64 |
| 4 | Oil, Evap. 40 min | 0.39 | 0.04 | 0.06 | 2.41 | 6.96 | 2.06 | 42.5 | 0.54 | 2.45 | 0.03 | 0.16 | 0.77 | 1.85 | 2.57 | 1.18 | 0.43 | 2.18 | 0.61 |

* not measurable owing to poor resolution of peaks

\+ analyses were of a C6+ distillate from the condensate

++ condensate suffered evaporation and fractional losses upon collection. Compositional ratios unreliable.

Headings A,B,X, etc. are defined in Table 1

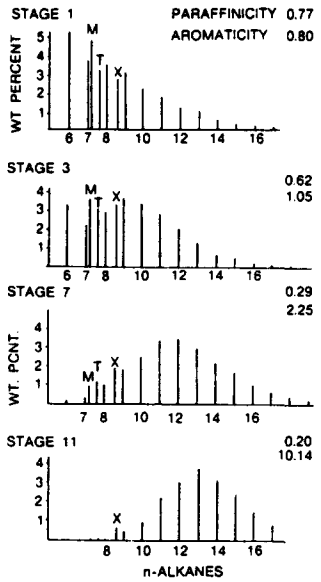


Fig. 4. Simulated gas chromatograms of condensates from Experimental Series 3. M, methylcyclohexane; T, toluene; X, $m+p$-xylenes. Paraffinicity defined as $n$-$C_7$/M; aromaticity as X/$n$-$C_8$.

$C_6$–$C_{10}$ region, and then progressively skewed towards higher molecular weights, with increasing excesses (over adjacent alkanes) of benzene (B), toluene (T), meta-, and para-xylene (X), as well as of methylcyclohexane (M). The final value of the ratio toluene/$n$-heptane shows an 8.2-fold increase over the initial value, xylenes/$n$-octane a 12.7-fold increase, while paraffinicity, $n$-heptane/methylcyclohexane, decreases 3.9-fold (Table 4). The characteristic deltoid profile of depleted petroleums is seen at and beyond Stage 5. The dominent normal alkane migrates progressively to $n$-$C_{13}$, and the "superabundance", or excess of benzene, toluene, the xylenes and methylcyclohexane over adjacent normal-alkanes, increases. Such superabundances of light aromatics (B > 1) will be demonstrated for oils from numerous basins.

Figure 5 is a summary diagram showing the relationships of toluene/$n$-heptane (aromaticity, B) and $n$-heptane/methylcyclohexane (paraffinicity, F) in Experiments 1, 2, and 3. Conceptual tie-lines joining parent and daughter compositions, or the sequential series of daughter products in Series 3, generate an imaginary suite of curves which represent alteration pathways. If paraffinicity is initially high it is rapidly diminished, aromaticity increasing slowly. If aromaticity is originally high, it increases rapidly, paraffinity decreasing asymptotically. In subsequent sections aromaticity and paraffinicity data are presented which relate to suites of oils and condensates having wide geographic and stratigraphic distributions. The data are distributed along paths parallel to, or coincident with, the Experimental Series 2 and 3 trends, and are therefore interpreted in terms of evaporative fractionation.

Experimental Series 4 was performed to determine the comparative effects of evaporation at room temperature and evaporative fractionation at elevated pressure and temperature (Table 4). Even after unrestricted evaporation for 40 min, losses of $C_{9+}$ compounds are modest, although the lightest components are almost completely removed. Fractionation is evident in the sharp increase in benzene/$n$-hexane, but is not accompanied by an increase in xylene/$n$-octane. Several criteria are thus indicated for distinguishing normal evaporation from evaporative fractionation (conceived of as a reservoir process).

## DISCUSSION

Evidence of evaporative fractionation processes affecting oils and gas-condensates in nature will be presented. Evidence of three types is available: (1) compositional ratio data for gasoline fractions of cogenetic sets of oils and condensates which exhibit increasing levels of aromaticity and concommitantly decreasing paraffinicity; (2) whole-oil chromatograms showing light end depletion accompanied by anomalously high levels of light aromatics and naphthenes; and (3) anomalous aromatic profiles based on U.S. Bureau of Mines routine Oil Analyses. The latter are discussed in a companion publication (Thompson, 1987) and are not reviewed further here.

### *Light hydrocarbons of unaltered oils*

Before discussing the nature of oils believed to be altered by evaporative fractionation, the gasoline composition of the starting materials (pristine oils of

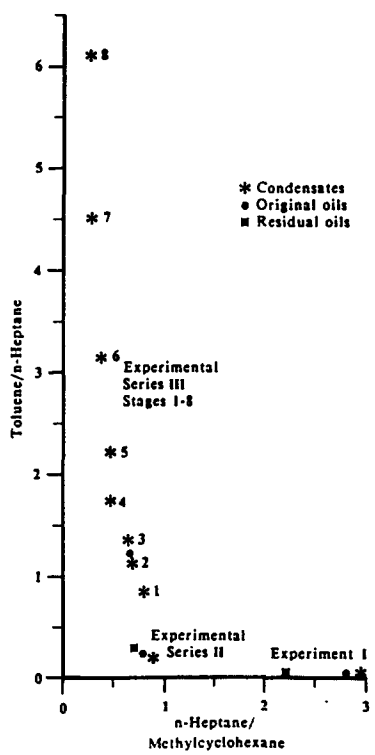


Fig. 5. Aromaticity (B) versus paraffinicity (F), Experimental Series 1, 2, and 3.

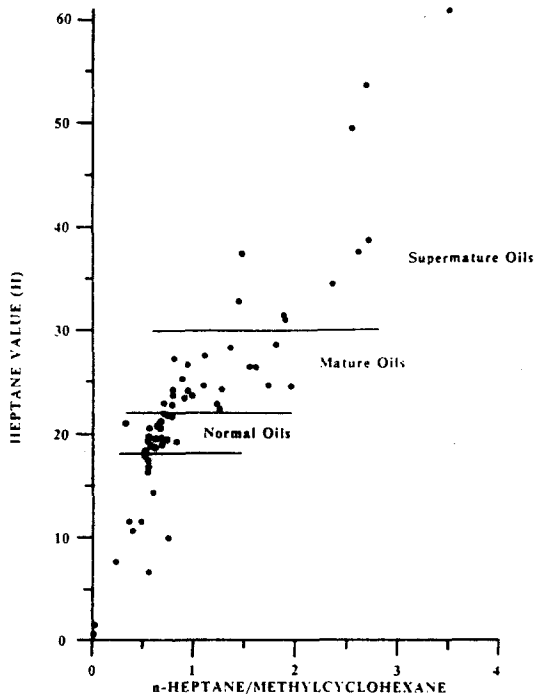


Fig. 6. Relationship of heptane value (H) and ratio *n*-heptane/methylcyclohexane (F) in 76 North American oils, showing classification. Data from Thompson (1983).

varying levels of thermal maturity) will be reviewed. Three categories of unaltered oils termed normal, mature, and supermature, were defined in terms of light hydrocarbon paraffinicity (Thompson, 1983). Classification was based upon parameters designated the heptane and isoheptane values (Table 1) which are indices of maturity (Thompson, 1979). The ratio employed to assess paraffinicity throughout the present study, *n*-heptane/methylcyclohexane (F), is strongly covariant with heptane value data (Fig. 6) and therefore is also a maturity indicator. Normal oils possess, by definition, heptane values between 18 and 22, generally associated with values of F between 0.5 and 0.8, representing equivalent vitrinite reflectance levels of approximately 0.86–1.05%. Mature oils, defined by heptane values between 22 and 30, possess values of F between 0.8 and approximately 1.5; supermature oils exhibit heptane values greater than 30, F greater than 1.5. No vitrinite reflectance control exists for high paraffinicities developed in petroleum reservoirs other than the two data shown in Table 5 for the Adorf Z1 and Z5 condensates. These have heptane values of 43.6 and 44.3, respectively, and reservoir $R_0$ values of 1.6–1.8%.

In Fig. 7 a group of unmodified normal oils representing (1) Tertiary reservoirs in the Cook Inlet area (Alaska); (2) Lower Cretaceous reservoirs in the Denver Basin (Colorado and Nebraska); and (3) Upper Cretaceous reservoirs in the Powder River Basin (Wyoming), are characterized in terms of B and F (data from Thompson, 1983). The oils represent a variety of Mesozoic source rocks, but exhibit a remarkable original uniformity of composition. The Powder River Basin oils occur in a region approximately seventy miles in length. Analyzed oils from the eastern Denver Basin and adjacent Nebraska have migrated many tens of miles (Clayton and Swetland, 1980) through faults, fractures, and carrier beds, without compositional modification. These groups were previously described as exhibiting "geographic homogeneity"; they may also be termed pristine. They are evidently unchanged from the condition in which they left the source rock. The original, modal, value of B is approximately 0.25.

Table 5. Summary of distribution of aromatic hydrocarbons in representative oils

| FIELD, LOCATION | BUR. OF MINES ANALYSIS | TYPE OF OIL | VOLUME PERCENT AROMATICS* BP 50°-210°C Fracs. 1-7 | BP 211°-420°C Fracs. 8-15 | TOTAL AROMATICS |
|---|---|---|---|---|---|
| Hendricks, Tx | B54137 | Unfractionated | 2.9 | 10.9 | 13.8 |
| Darius, Iran | B69085 | Unfractionated | 3.9 | 6.4 | 10.3 |
| Kawkawlin, MI | B57056 | Unfractionated | 2.1 | 9.0 | 11.1 |
| North Smyer, TX | B64112 | Unfractionated | 3.8 | 9.0 | 12.8 |
| Beaver Lodge, ND | B58012 | Fractionated | 6.9 | 8.2 | 15.1 |
| Lee Harrison, TX | B59054 | Fractionated | 7.6 | 8.2 | 15.8 |
| South Houston, TX | -- | Biodegraded | 1.4 | 19.3 | 20.7 |

*Data of Martin *et al.*, 1963; Fractions 1-7 represent the gasoline range.

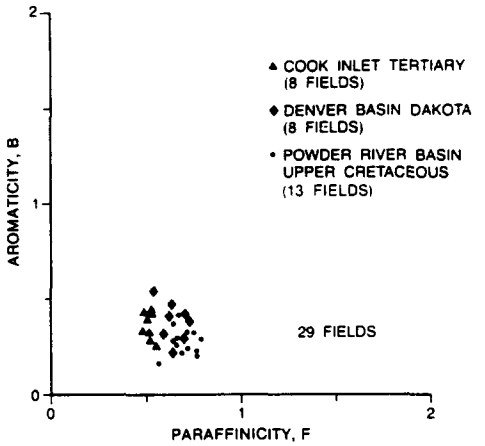


Fig. 7. Aromaticity (B) versus paraffinicity (F) for three geographic-stratigraphic sets of North American oils of normal maturity. Oils are regarded as pristine. Data from Thompson (1983).

*Gasoline data evidencing evaporative fractionation*

Figure 8 (data from Thompson, 1983) represents three groups of oils from (1) Carboniferous reservoirs in the central and eastern Williston Basin of North Dakota and eastern Saskatchewan; (2) Tertiary reservoirs in the Santa Maria Basin and Santa Barbara Channel of California; and (3) reservoirs on the North Slope, Alaska. Their compositional variation is attributed to evaporative fractionation on the basis of three lines of evidence. Firstly, if pristine oils cluster on a B–F diagram, then most of the oils of Fig. 8 are altered. Secondly, a process capable of generating the requisite alteration vectors in terms of a B–F diagram was demonstrated experimentally. Thirdly, recognized oil modification processes discussed below, generate alteration vectors having orientations distinctly different from those of Fig. 8. The effects of thermal alteration, and water-washing (extraction of light aromatics upon migration), are illustrated in a subsequent section. The effects of biodegradation upon gasoline composition were documented by Winters and Williams (1969), Welte *et al.* (1982), as well as by Thompson (1983). The compositional changes in a North Slope oil resulting in the values B, 0.25 and F, 0.36 (lower left of Fig. 8) are attributable to biodegradation. The principal trend of the data of Fig. 8 is not attributable to any previously recognized alteration process, but is predictable in terms of evaporative fractionation.

The unaltered oils shown in Fig. 8 are designated mature. F lies between 1.2 and 1.4, associated with heptane values between 22 and 28. These maturities are higher than those depicted in Fig. 7, and in fact approach levels designated supermature ($F > 1.5$, $H > 30$). However, aromaticity appears to be approximately equal in the two sets, B averaging 0.25. The oils of Fig. 8 exhibit diminishing values of the ratio F (to approximately 0.75) with increasing aromaticity which could lead to an erroneous designation of normal maturity in the highly aromatic oils. This observation emphasizes the fact that evaporative fractionation results in spuriously low maturity designations in affected oils and their daughter condensates. Retrogressive changes in maturity indicators based on paraffinicity take place.

*Heavy ends unchanged by fractionation*

The relationship between the aromaticity of the gasoline range when increased by fractionation and the aromaticity of the remainder of the oil has not been adequately determined. It would be predicted that the heavy ends are not modified. Limited data are provided by the mass spectrometric analyses of fractions of seven oils by Martin *et al.* (1963). Table 5 summarizes the distribution of nine classes of aromatic hydrocarbons. Bureau of Mines analyses are available for oils from six of the fields represented. They provide evidence that two of them, Beaver Lodge and Lee Harrison, have undergone evaporative fractionation. This is indicated by their aromatic profiles which show enhanced levels of alkylbenzenes in fractions 6 and 7. The profiles adopt a sigmoid form in these circumstances, rather than a smooth curvilinear one (Thompson, 1987). This enrichment in alkylbenzenes in the gasoline-range is also evident in the data of Martin *et al.* for the two oils. However, aromatics in the mid-range and heavy ends appear to be approximately equal in all of the oils, suggesting that evaporative fractionation does not significantly alter the heavy ends. The fractionated oils, in the cases evaluated, are higher in total aromatics than the unfractionated ones.

*Evaporative condensates*

Evaporative fractionation of oil occurs upon the generation of a mobile gas phase (a single-phase fluid) bearing substantial volumes of light and intermediate molecular weight hydrocarbons in solution.

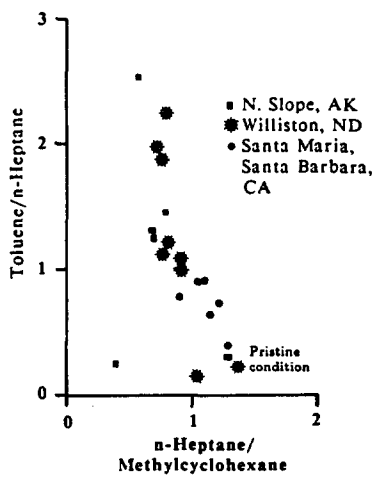


Fig. 8. Aromaticity (B) versus paraffinicity (F) for North American oils interpreted as exhibiting evaporative fractionation. Data from Thompson (1983).

Table 6. Gasoline and heavy end data, condensates from the Zechstein Basin, northwest Germany, and from sub-Alpine basins, southern Germany and northern Italy

| Number | Basin | Formation (Age) | Vitrinite Rm% | Depth (m) | Well | Gasoline Parameters | | | | | | | | | C15+ | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | A | B | X | C | I | F | H | U | R | $\delta^{13}$C,o/oo | δD,o/oo |
| 1 | Zechstein | Ca2* | 0.6 | 1985 | Weilen Z2 | 0.80 | 0.58 | -- | 0.80 | 3.01 | 0.74 | 25.2 | 2.47 | 2.79 | -25.3 | -95 |
| 2 | Zechstein | Ca2 | 0.7 | 2230 | Uelsen Z2 | 0.81 | 0.69 | -- | 0.77 | 3.19 | 0.73 | 25.1 | 2.47 | 2.60 | -26.3 | -106 |
| 3 | Zechstein | Ca2 | 0.8 (1.1)+ | 2297 | Ratzel Z1 | 0.88 | 0.92 | -- | 0.72 | 3.01 | 0.61 | 22.3 | 2.33 | 2.41 | -26.0 | -109 |
| 4 | Zechstein | U. Carboniferous | 0.8 | 2654 | Ratzel Z4 | 0.71 | 0.34 | -- | 0.71 | 3.15 | 0.58 | 21.4 | 2.08 | 2.18 | -27.0 | -127 |
| 5 | Zechstein | Ca2 | (1.1) | 2600 | Emlichheim Z4A | 3.37 | 2.14 | -- | 0.69 | 2.99 | 0.73 | 28.8 | 3.65 | 4.09 | -25.2 | -- |
| 6 | Zechstein | Ca2 | (1.6) | -- | Emlichheim NZ9 | 1.24 | 1.20 | -- | 0.62 | 3.23 | 0.58 | 21.1 | 2.18 | 2.01 | -25.9 | -- |
| 7 | Zechstein | U. Carboniferous | (1.6) | 2716 | Emlichheim NZ3 | 3.76 | 1.78 | -- | 0.42 | 2.91 | 0.43 | 21.7 | 3.27 | 3.25 | -26.7 | -- |
| 8 | Zechstein | Ca2 | 1.3 (1.1) | 2750 | Kalle Z6 | 0.32 | 0.49 | -- | 1.61 | 3.12 | 1.63 | 37.9 | 2.12 | 4.14 | -24.6 | -57 |
| 9 | Zechstein | Ca2 | 1.6 (1.0) | 2850 | Adorf Z1 | 1.59 | 1.13 | -- | 2.11 | 3.58 | 2.62 | 43.7 | 2.54 | 4.17 | -24.6 | -75 |
| 10 | Zechstein | Ca2 | 1.8 (1.0) | 2765 | Adorf Z5 | 1.53 | 1.06 | -- | 2.17 | 3.60 | 2.71 | 44.3 | 2.59 | 4.18 | -24.4 | -62 |
| 11 | Molasse | Oligo.-Miocene | <0.6 | ~2000 | Breitbrunn 2 | 1.05 | 5.09 | -- | 0.36 | 0.23 | 0.32 | 10.4 | 0.38 | 2.95 | -- | -- |
| 12 | Molasse | Oligo.-Miocene | <0.6 | ~2000 | Breitbrunn 3 | 0.40 | 3.82 | -- | 0.37 | 0.22 | 0.29 | 8.76 | 0.28 | 2.37 | -- | -- |
| 13 | Molasse | Oligo.-Miocene | <0.6 | ~2000 | Breitbrunn 9 | 0.67 | 1.61 | -- | 0.77 | 0.55 | 0.70 | 19.20 | 0.96 | 3.17 | -- | -- |
| 14 | Molasse | Oligo.-Miocene | <0.6 | ~2000 | Breitbrunn C1 | 0.25 | 2.30 | -- | 0.28 | 0.17 | 0.23 | 7.3 | 0.29 | 2.52 | -- | -- |
| 15 | Po (Italy) | L. Jurassic | -- | 5500 | Molossa 11 | 0.28 | 0.40 | -- | 1.71 | 6.42 | 1.48 | 32.9 | 1.78 | 2.29 | -- | -- |

*Ca2, Stink Kalk, Permian

+Teichmuller et al., 1979

This gas must, it appears, either exit from the reservoir system at the surface of the earth, or be trapped in shallower reservoirs. It follows logically that a region possessing abundant fractionated oils should exhibit plentiful accumulations of gas-condensates. Both of these features are present in the Gulf of Mexico region, but GC analyses of gasoline-range hydrocarbons with which to assess the nature of the fluids are presently unavailable for publication.

Gasoline analyses are, however, available for a group of gas-condensates occurring in the Zechstein Basin of northwest Germany, principally in the Permian Stink Kalk, a bituminous limestone and probable source formation designated the Ca2 horizon of the Middle Zechstein Series (Schoell, 1984). Complex geological structure facilitates the occurrence of almost identical gas-condensates in the Upper Carboniferous, evidently by migration. Table 6 presents relevant analytical data prepared in cooperation with M. Schoell who also isotopically characterized the non-condensable gaseous components and provided the samples.

A second group of condensates with available gasoline analyses comes from sub-Alpine basins in southern Germany and northern Italy (Table 6). Non-associated gas is produced from Miocene, Oligocene, and pre-Tertiary reservoirs. The section also produces oil. The Breitbrunn field (Table 6) is in the Molasse Basin of southern Germany. The Molossa field is in the Po Valley Basin, northern Italy. Both areas are described by Schoell (1984), who provided the condensate samples.

Figure 9 represents the aromaticity and paraffinicity parameters, B and F, of the German and Italian condensates. All condensates except four (Molossa, Kalle, Adorf Z1 and Z5) exhibit the same relationships as were created experimentally. An interpretation based on the evaporative fractionation of precursor oils is therefore postulated. The model suggests that the precursors were of slightly lower paraffinicity than the most paraffinic condensates, that is, that the precursor oils were of normal maturity (F = 0.5–0.8). The four condensates named above are exceptions which appear to be of high maturity but otherwise unaltered, as described further below. However, the majority can be explained in terms of progressive evaporative fractionation.

*Thermal condensates*

The conventional understanding of gas condensates is that, almost without exception, they are thermal in origin, implying that they are generated by the cracking of liquid oil, particularly at vitrinite reflectance levels in excess of 1.2%. The sections above indicate that many gas-condensates are formed by merely physical processes involving evaporative fractionation. A source of gas at depth in invoked, possibly directly from source rocks, or due to the cracking of oil in deep accumulations. However, a few gas-condensates possess the paraffinicities of supermature oils, but occurring in the gas phase are truly thermal condensates. Such are the Adorf Z1, Adorf Z5, and Kalle Z6 Zechstein condensates. Supermature oils possess heptane values greater than 30, isoheptane values greater than 2.0, and values of the paraffinicity ratio F greater than 1.5. Such values occur in these three condensates (Table 6) which are found in the deepest reservoirs in the Ems area, exhibiting vitrinite reflectances of 1.3–1.8%, levels of rapid thermal cracking. Both Faber *et al.* (1979) and Müller (1984) have shown that the Middle Zechstein carbonates include petroleum source beds. As the Adorf and Kalle gas-condensates are reservoired within their source unit, observations of stratal maturity can be applied, at least as minima, to the contained fluids.

Further evidence of the highly mature state of the three condensates is provided by their isotopically heavy nature, in terms of $\delta^{13}C$ and $\delta D$. Thermal maturation enriches residual fluids in $^{13}C$ and D by the generation of isotopically light methane. In the Adorf and Kalle condensates, $\delta^{13}C$ averages $-24.5$ per mil, and $\delta D$, $-65$ per mil, while comparable averages for the other members of the suite reported by Schoell (1984) are $-25.6$ and $-101$ per mil, respectively. The Molossa condensate is closely similar to these three Zechstein cases in gasoline aromaticity and paraffinicity. Together, the four samples demonstrate that increase in light end paraffinicity is accompanied by increase in aromaticity during thermal cracking. A similar observation appears to have been made previously only by Sawatzky *et al.* (1977). They noted that increasing maturity causes a dra-

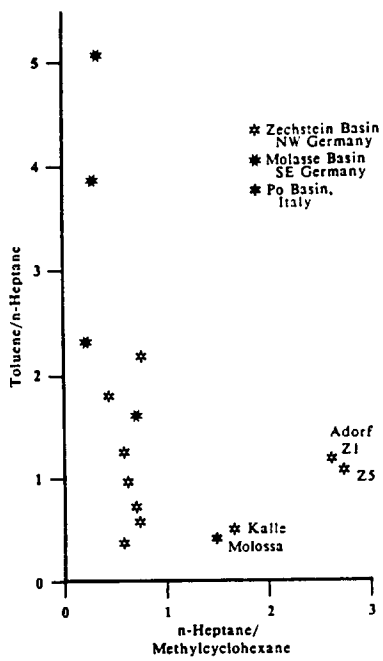


Fig. 9. Aromaticity (B) versus paraffinicity (F) for fifteen gas-condensate liquids. Molossa, Kalle, Adorf Z1, and Z5, are interpreted as unfractionated thermal condensates, the remainder as originally normal or mature evaporative condensates.

matic increase in alkylbenzenes and benzene in Canadian East Coast oils. On the contrary, heavy end aromaticity decreases during maturation, as shown by Tissot and Welte (1984).

*Oils and gas-condensates with spurious characteristics of immaturity*

Progressive increase in the paraffinicity of gasoline-range extracts of sedimentary rocks can be traced from 180°F to over 380°F stratal temperatures ($R_o$ 0.45% to $R_o$ 1.95%) in the Gulf Coast Miocene. Heptane values increase linearly from unity to 35, and isoheptane values increase exponentially from approximately 0.5 to over 6 in aromatic, Type III, kerogens (Thompson, 1979). Isoheptane values increase less rapidly in Type II, aliphatic, kerogens. These scales were related to the generation of oil in 1983, and it was suggested that the lowest heptane value occurring in a widespread, uniform suite of oils was 18. Lower paraffinicities were attributed to biodegradation. This work shows that progressive fractionation can reduce initially high paraffinicities to low values, evidenced clearly by Experimental Series 3 (Table 4), the Williston basin data (Fig. 8), and the Breitbrunn condensates (Table 6). It is to be added, however, that a small proportion of oils are released at low levels of source rock maturity, for example, certain of those of the San Joaquin Valley, California. Here, low levels of paraffinicity are accompanied by high levels of pristane, phytane, and steranes, the latter in their biological configurations, without evidence of biodegradation. All of these features combine to suggest immaturity.

It is evident that interpretations of indices of paraffinicity in fluids (H, I, and F) must be made in conjunction with those of indices of aromaticity (A, B, and X). High values of the latter may evidence fractionation. The paraffinicity of fractionated liquids is anomalously low, in relation to their thermal history. A regionally-representative suite of analyses will frequently reveal the original maturity of the pristine oils or condensates of the area when plotted on a B versus F diagram, as shown in Figs 8–10.

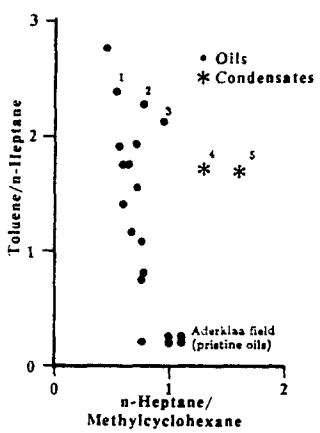


Fig. 10. Aromaticity (B) versus paraffinicity (F) for oils of the Vienna Basin, data of Welte *et al.* (1982). Cases 1–5 represent fluids from Triassic reservoirs wherein the gas-condensates are probably derived from the oils.

Several published studies (Snowdon and Powell, 1982; also Nissenbaum *et al.*, 1985) have employed low observed values of indices of paraffinicity (heptane and isoheptane values) to aid in the definition of fluids which were termed *immature condensates*. Convincing evidence of the absence of biodegradation should accompany such claims, because the process lowers paraffinicity. Furthermore, present knowledge suggests that condensates should be reexamined for evidence of fractionation. Paraffinicities attributed to immaturity by Snowdon and Powell (H, 8–15; I, 0.5–1.75), and by Nissenbaum *et al.* (H, 7.1; I, 0.12) could have been generated by fractionation of a mature oil. Snowdon and Powell (1982) suggested that plant resins associated with Type III kerogens are the source of "immature" condensates. Recent hydrous pyrolysis studies by Lewan and Williams (1987) indicate strongly that resins do not generate naphthenic petroleums at low maturity levels. Ejedawe (1986) drew the opposite conclusion for certain Niger delta wells but presented no detailed analytical evidence.

*Vienna Basin oils and condensates*

Welte *et al.* (1982) provided a body of analytical data relating to 57 oils and 3 condensates from the Vienna Basin, Austria, an intra-Alpine subsidence, adjacent to, and east of, the Molasse Basin. The majority of samples derive from the Miocene–Pliocene basin fill, up to 5 km in thickness. Eight samples, including the condensates, are from intensely folded Upper Cretaceous and Upper Triassic strata, deformed by the Alpine orogeny, occurring beneath a major unconformity. Sterane and triterpane patterns in the oils demonstrated that all of the oils, with one exception, derive from a single, unidentified, Mesozoic source. The majority of oils are biodegraded. The "unaltered" oils, as recognized by Welte *et al.*, are plotted in Fig. 10.

Figure 10 suggests an interpretation of the composition of the oils in terms of evaporative fractionation. They are regarded here as variously enriched in toluene and methylcyclohexane by this process. The oils appear to derive from a pristine stock represented in the Aderklaa field. These are mature oils (average F, 1.1; B, 0.24). The alteration pathway in Fig. 10 largely coincides with that observed for numerous Zechstein condensates, as well as that of Experimental Series 3. The gas chromatograms of these oils illustrated by Welte *et al.* lack resolution below approximately $n$-$C_{11}$. However, several (for example, Schönkirchen Tief 38 and Rabensburg U4) are clearly deltoid, the dominant normal-alkane in both being $n$-$C_{20}$. These features resemble those of the residual oil and late-stage condensates of Experimental Series 2 and 3, respectively, also those of the representative Gulf Coast oil illustrated below.

*U.S. Gulf Coast oils and condensates*

A novel interpretation of U.S. Bureau of Mines Routine Oil Analysis Data (Thompson, 1987) indicates that over 75% of the oils in Gulf Coast Tertiary reservoirs are depleted in light ends, and are enriched in light aromatic hydrocarbons, that is, they are evidently affected by evaporative fractionation. Gas chromatographic evidence of the phenomenon is illustrated in Fig. 11. Oils closely similar to that of Bayou Sale, and which reproduce the features of Experimental Series 2 and 3 condensates and oils, are commonplace in the region. Relevant gas chromatographic data will be the subject of a future paper.

*Allochthonous methane*

The mechanism of evaporative fractionation is believed to be represented by the experiments described above. An excess of methane was employed, suggesting that fractionated reservoirs in nature might contain allochthonous methane: gas added through fractures in amounts exceeding the complement generated with the oil. Schoell (1984) presented isotopic evidence ($\delta^{13}C$ and $\delta D$) of the partially allochthonous nature of the methane associated with the Zechstein Ca2 condensates, attributing part to highly mature Upper Carboniferous coals beneath the Zechstein Series. This concept was initially proposed by Boigk *et al.* (1976). It is suggested here that ethane in the Ca2 fluids is entirely allochthonous on the basis of $\delta^{13}C$ values. Schoell quoted data for 15 condensates exhibiting an average $\delta^{13}C$ of $-25.51 \pm 0.76$ per mil for the $C_{15+}$ fraction. The methane in six of them for which data were provided averaged $-28.15 \pm 1.88$, while ethane in the same gases averaged $-23.50 \pm 1.22$ per mil. It is not possible for ethane to be richer in $^{13}C$ than the carbon pool from which it is derived, thereby excluding the condensates as a source. This is in accord with the suggested mechanism, involving both allochthonous methane and ethane.

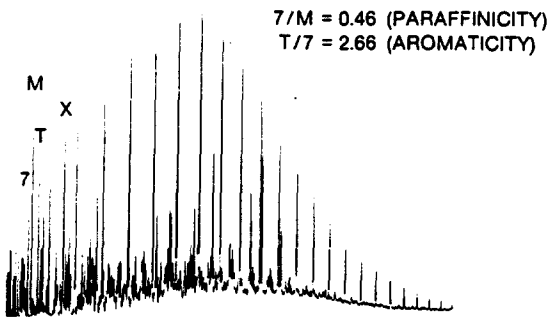


Fig. 11. Gas chromatogram of oil from Bayou Sale field (Miocene), Louisiana. Deltoid profile and "superabundances" of toluene (T) and $m+p$-xylene (X) reproduce features of Experimental Series 3 and are attributed to evaporative fractionation. Features are characteristic of the majority of Gulf Coast Tertiary-reservoired oils. Methylcyclohexane, M; $n$-Heptane, 7.

Further evidence of allochthonous methane in fractionated oils is available in the case of the Vienna Basin. Schoell (*supra cit.*) provided $\delta^{13}C$ (methane) data for several fields from which oils were analysed by Welte *et al.* (1982), although there is no correspondence by well number. Most of the analysed oils of the Vienna Basin (Fig. 10) are believed to have originally possessed values of B and F close to those of the Aderklaa field, with the probable exception of the Triassic Schönkirchen reservoirs (cases 1–5). The majority are therefore construed as being of equal actual maturity. They should be accompanied by methanes representing a consistent level of thermal cracking and possessing approximately equal values of $\delta^{13}C$. However, Schoell reported methanes ranging from $-32.2$ to $-42.8$ per mil in the Tertiary reservoirs of Schönkirchen, Matzen, and Aderklaa. The wide range demonstrates the allochthonous nature of part of the methane in fields possessing fractionated oils. Schoell (*supra cit.*) also provided isotopic data for the methane of a Breitbrunn gas-condensate from the Molasse Basin. $\delta^{13}C$ was $-67.7$ per mil, $\delta D$, $-192$ per mil. Both values are characteristic of bacterial methane, as Schoell (1983) demonstrated. The gas is clearly allochthonous in relation to the condensate.

*Hypothetical mechanisms*

Evaporative fractionation appears to entail two basic mechanisms if the experiments described above simulate natural phenomena, as seems to be the case. Firstly, the fractionating process takes place at the moment of segregation of a saturated gas phase from gas-saturated liquid. Secondly, and subsequently, a process of separation ensues, with migration of the gas phase away from the parent liquid. There is no factual information as to the mode of operation of either segregation or separation steps.

Several published hypotheses bear on the separation process. The earliest was that of Gussow (1954) who described "differential entrapment" of oil and gas in a series of shelf anticlines. He postulated oil and gas migrating simultaneously. When structurally lower traps are filled to the spill point oil can no longer enter, but gas will be able to do so, displacing oil updip. Eventually the lower traps will contain only gas, in fact, a gas-condensate fluid in phase-equilibrium with the oil. This is a realistic model, but not one which suggests much interchange or variability in fluid contents.

Schowalter (1979) expanded these concepts to include a series of permeability-limited stratigraphic traps in a process which he termed "leak differential entrapment". Stratigraphic traps were seen as a series of displacement-pressure barriers which would hold a given maximum hydrocarbon column, and then leak updip. The earliest leakage fluid in this instance is gas, from the apices of the traps. Once again, saturated gas is separated from equilibrated oil. This mechanism has the appeal of versatility, and applica-

bility to deltaic sequences, where all sand bodies are ultimately lensoid. Silverman (1965) described "separation migration". For this process to take place, separate oil and gas phases must already exist in the trap. Fault leakage of the gas cap alone was visualized, with retrograde condensation of the migrating gas in a shallower trap. Two fractionating steps are represented here. There appears to be no other published evidence of the natural occurrence of retrograde condensate liquids in reservoirs.

Segregation processes do not appear to be addressed in the literature. An early opportunity for segregation occurs during initial secondary migration. Presumably, oil leaving a source unit is gas-saturated. Within a carrier bed, as pressure and temperature decrease, degassing with fractionation will take place. This mechanism provides, however, only a limited range of pressure and temperature conditions for degassing, and therefore a limited range of compositions. To provide the element of randomness of pressure and temperature conditions for segregation, whence the opportunity for tremendous variability in composition of fractionated cogenetic oils, as found in the Gulf Coast, a fault-driven model was proposed (Thompson, 1987). In summary, it is believed that a random fault or fracture, connecting a gas-saturated oil accumulation and a shallower trapping bed, generates a low pressure region in its vicinity in the oil accumulation. Pressure is believed to equalize along the open fracture, at a level intermediate between that at its upper and lower limits. In the oil accumulation this might be a pressure below the bubble point. If so, degassing ensues immediately in the vicinity of the fracture, initiating two-phase flow.

In two-phase flow the rates of simultaneous flow of oil and gas in a porous medium differ substantially, and are determined by relative permeabilities and relative viscosities. Concerning the former, Arps and Roberts (1955) found that, on the average, for sixteen productive sandstones, gas relative permeability was equal to that of oil at 30% gas and 70% oil saturation. As gas viscosity is generally approximately one percent of that of oil, gas flow in these circumstances would exceed oil flow by a factor of one hundred. With increasing gas saturation there is rapid decrease in oil flow. At 50% gas and 50% oil saturation, oil flow diminishes to one part in one thousand of net flow.

These reservoir engineering principles (Craft and Hawkins, 1959), can be applied to a hypothetical fault breaching a gas-saturated oil sand. They suggest that the fault pathway would be an avenue of gas flow only. The liquid phase would be substantially trapped in the reservoir because of relative permeability and relative viscosity phenomena. The release of saturated gas from an oil accumulation is conceived of as the vital fractionating step required to drive the process of evaporative fractionation. The randomness of a fault mechanism is appealing because of the variety of compositions which could be produced from a pristine oil by variations in pressure and temperature in the faulted reservoirs. The possibility of introducing relatively dry gas from depth adds the opportunity for further fractionation steps.

*Frequency of occurrence of evaporative condensates*

As described in the introduction, the gas-condensates of the San Juan Basin, New Mexico, are largely of evaporative origin. The majority of those in the U.S. Gulf Coast Tertiary appear to be similarly generated, on the basis of limited evidence (Thompson, 1987). An investigation of 126 oils and condensates of the Dnieper-Donets Depression (Korchinskaya and Novosiletskiy, 1978) revealed a wide range of values of a thermal alteration index, defined as the ratio of the sum of paraffins-plus-aromatics to naphthenes in the gasoline range. At each level of the index, which decreased regularly away from the basin center, there occurred both oils and condensates. This suggests gas-condensate generation by a physical process, not thermal cracking. Powell (1979) attributed the generation of gas-condensate encountered in the well Snorri J-90 on the Labrador Shelf of Canada to separation from an oil during migration, according to the model of Schowalter (1979).

In summary, it is suggested that large numbers of gas-condensate accumulations are the products of evaporative fractionation, especially those in sediments of maturity levels within the range of 0.5–1.2% vitrinite reflectance, the oil window. Relevant statistics are not yet available.

## SUMMARY

The concepts of this study are summarized in Fig. 12 in terms of alteration vectors on a B–F diagram. Twelve regions of available data, representing single fluids or groups, are indicated by values of the ratios toluene/*n*-heptane (B), and *n*-heptane/methylcyclohexane (F). Fluid compositions 1–5 represent experimentally generated changes wherein the removal of a saturated gas phase was the causal mechanism of change. The processes are jointly termed evaporative fractionation (vectors A). Vectors $6 \rightarrow 7$ and $8 \rightarrow 9$ represent sequences of observed compositions of oils and condensate in four basins (Zechstein, North Slope, Williston, and coastal California). These and other observations (cluster 10, data of Fig. 7) are believed to infer that all source rocks generate oils of nearly identical paraffinicity and aromaticity parameters in the gasoline range, firstly in pristine oils. Close similarities are preserved during subsequent alterations. Vectors $6 \rightarrow 7$ and $8 \rightarrow 9$ are attributed to evaporative fractionation.

Evaporative fractionation appears to be a major mechanism of generation of gas-condensate fluids within the oil-window, generally recognized as occurring between 0.5 and 1.2% vitrinite reflectance levels. Such are the condensates of the San Juan Basin, also

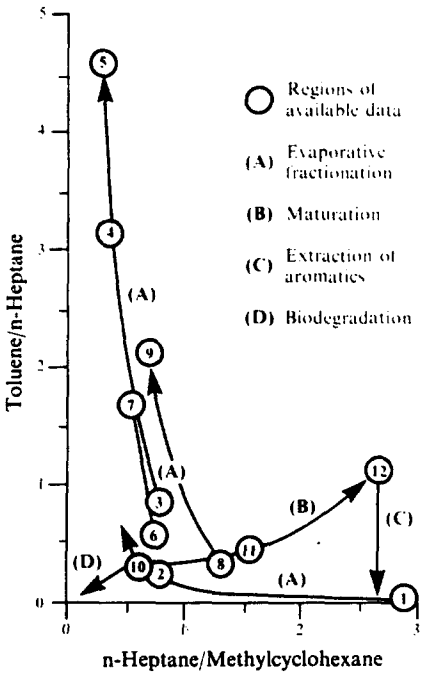


Fig. 12. Summary diagram representing alteration vectors of four types: (A) evaporative fractionation; (B) maturation; (C) extraction of light aromatics by water; and (D) biodegradation. Data groups are defined in text.

those of the Zechstein and Molasse basins. Limited published data (Thompson, 1987) suggest that those of the U.S. Gulf Coast are principally of evaporative origin. In the generation of gas-condensates by this mechanism, allochthonous methane would be required after the exhaustion of the gas initially present in solution in a given oil reservoir. Partial derivation of the Zechstein gas from Upper Carboniferous coals at depth provides an example of allochthonous methane. Others are quoted.

Unaltered pristine oils of normal maturity, $F < 0.8$, form a tight cluster on a B–F diagram (group 10, in Fig. 12, representing three basins). It is postulated that thermal transformation of oils in deep reservoirs leads to progressive cracking, with increasing paraffinicity and, as first documented here, slight increase in aromaticity (mature oils, $F = 0.8$–$1.5$, Groups 8 and 11, Figs 8 and 9, respectively). Advanced maturation without loss of light ends leads to supermature oils and condensates. The latter are exemplified by the Adorf condensates, Group 12, $F > 1.5$, occurring in reservoirs of elevated vitrinite reflectance levels (1.6–1.8%). Substantial increases in aromaticity accompany late stage maturation, indicated by vector (B). In fact, superabundances of light aromatics are generated by thermal cracking, as well as by fractionation, leading to values of ratios B and X greater than unity. It is suggested, as put forward by numerous others (references of Silverman, 1965; also Welte *et al.*, 1982), that aromaticity is frequently diminished by extraction of low molecular weight aromatic compounds in connate or meteoric waters during migration, indicated schematically by vector (C). Analysis (1) represents the Sulfur Bluffs oil of Experiment 1, interpreted as supermature and stripped of light aromatics.

It is also suggested that thermal condensates are the analogs of supermature oils, the products of advanced cracking. They appear to be of rare occurrence in unaltered form. Condensates which have been termed immature, in part on the basis of paraffinicity levels below those of normal oils ($F = 0.5$–$0.8$), might include, or entirely comprise, evaporative condensates of diminished apparent maturity.

A fourth alteration vector, D, represents biodegradation which results in extremely low values of both ratios, B and F. Data are given for North American oils in Thompson (1983), and in Welte *et al.* (1982) for those Vienna Basin oils which they designate as "altered".

*Acknowledgements*—This study derives from investigations initiated while the writer was associated with the Exploration and Production Research Department of Atlantic Richfield Company. Their support and release of experimental data is gratefully acknowledged. Thanks are expressed to W. V. Pasher, J. L. Haley and A. M. Rowe for assistance and valuable discussions; to J. C. Nicola for gas chromatography; and to Ms B. Koronka of Texas A&M University for careful preparation of the manuscript.

## REFERENCES

Arps J. J. and Roberts T. G. (1955) The effect of the relative permeability ratio, the oil gravity, and the solution gas-oil ratio on the primary recovery from a depletion type reservoir. *Trans. Am. Inst. Min. Metall. Pet. Eng.* **204**, 120.

Boigk H., Hagemann H. W., Stahl W. and Wollanke G. (1976) Isotopenphysikalische Untersuchungen zur Herkunft und Migration des Stickstoffs nordwestdeutscher Erdgase aus Oberkarbon und Rotliegend. *Erdol Kohle Erdgas Petrochem.* **29**, 103–112.

Craft B. C. and Hawkins M. F. (1959) *Applied Petroleum Reservoir Engineering*, 437 pp. Prentice-Hall.

Clayton J. L. and Swetland P. J. (1980) Petroleum generation and migration in the Denver basin. *Am. Assoc. Pet. Geol. Bull.* **64**, 1613–1633.

Connan J. and Cassou A. M. (1980) Properties of gases and petroleum liquids derived from terrestrial kerogen at various maturation levels. *Geochim. Cosmochim. Acta* **44**, 1–24.

Daubert T. E. (1983) Development of Gas Processors Association Data Bank of Selected Enthalpy and Equilibrium Values. Research Report 64, Gas Process. Assoc., Tulsa, Oklahoma.

Eilerts C. K. (1957) *The Phase Relations of Gas-Condensate Fluids*. Am. Gas Assoc., New York, 2 vols, 962 pp.

Ejedawe J. E. (1986) The expulsion criterion in the evaluation of petroleum source beds in the Tertiary Niger delta. *J. Pet. Geol.* **9**, 439–450.

Faber E., Schmitt M. and Stahl W. (1979) Geochemische Daten nordwestdeutscher Oberkarbon-, Zechstein- und Buntsandsteingase. *Erdol Kohle Erdgas Petrochem.* **32**, 65–70.

Gussow W. C. (1954) Differential entrapment of oil and gas—a fundamental principle. *Am. Assoc. Pet. Geol. Bull.* **38**, 816–853.

Hunt J. M. (1979) *Petroleum Geochemistry and Geology*, 617 pp. Freeman.

Korchinskaya I. A. and Novosiletskiy R. M. (1978) Types of oils and condensates and their distribution in the Dnieper-Donets Depression. *Pet. Geol.* **15**, 25–28.

Lewan M. D. and Williams J. A. (1987) Evaluation of petroleum generation from resinites by hydrous pyrolysis. *Am. Assoc. Pet. Geol. Bull.* **71**, 207–214.

Martin R. L., Winters J. C. and Williams J. A. (1963) Composition of crude oils by gas chromatography: geological significance of hydrocarbon distribution. *World Pet. Cong. 6th Frankfurt am Main, Proc.*, Vol. 5, pp. 231–260.

Müller E. P. (1984) Zur Genese von Erdolen in Karbonaten am Beispiel der Lagerstatten im Oberen Perm des Territoriums der DDR. *Z. Angewandte Geol.* **30**, 214–218.

Nissenbaum A., Goldberg M. and Aizenshtat Z. (1985) Immature condensate from southeastern mediterranean coastal plain, Israel. *Am. Assoc. Pet. Geol. Bull.* **69**, 946–949.

Powell T. G. (1979) Geochemistry of Snorri and Gudrid condensates, Labrador Shelf: Implications for future exploration. *Curr. Res. Part C Geol. Surv. Can.* **79-1C**, 91–95.

Price L. C., Wenger L. M., Ging T. and Blount C. W. (1983) Solubility of crude oil in methane as a function of pressure and temperature. *Org. Geochem.* **4**, 201–221.

Reid R. C., Prausnitz J. M. and Sherwood T. K. (1977) *The Properties of Gases and Liquids, Their Estimation and Correlation*, 688 pp. McGraw-Hill.

Rogers M. A. (1980) Application of organic facies concepts to hydrocarbon source rock evaluation. *10th World Pet. Congr. Proc.*, Vol. 2, pp. 23–30.

Rowe A. M. (1964) Application of a new convergence pressure concept to the enriched gas drive process. Ph.D. dissertation, Univ. Texas, Austin.

Sawatzky H., George A. E., Banerjee R. C., Smiley G. T. and Montgomery D. S. (1977) Maturation studies of Canadian east coast oils. CANMET Rep. 77-42, Cent. Can. Technol. Miner. Energy, Dept. of Energy, Ottawa, Canada, 15 pp.

Schoell Martin (1984) Wasserstoff und Kohlenstoffisotope in Organischen Substanzen, Erdolen und Erdgasen. Geol. Jahrb. Reihe D, 67, 164 pp., Bundesanstalt fur Geowissenschaften und Rohstoffe, Hannover.

Schoell Martin (1983) Genetic characterization of natural gases. *Am. Assoc. Pet. Geol. Bull.* **67**, 2225–2238.

Schowalter Tim T. (1979) Mechanics of secondary hydrocarbon migration and entrapment. *Am. Assoc. Pet. Geol. Bull.* **63**, 723–760.

Silverman S. R. (1965) Migration and segregation of oil and gas. In *Fluids in Subsurface Environments* (Edited by Young A. and Galley G. E.), pp. 53–65. Am. Assoc. Pet. Geol. Mem. 4.

Snowdon L. R. (1978) Organic geochemistry of the Upper Cretaceous/Tertiary delta complexes of the Beaufort-Mackenzie sedimentary basin, northern Canada. Ph.D. dissertation, Rice Univ., Houston.

Snowdon L. R. and Powell T. G. (1982) Immature oil and condensate—modification of hydrocarbon generation model for terrestrial organic matter. *Am. Assoc. Pet. Geol. Bull.* **66**, 775–788.

Stewart G., Todd A. C., Stamataki S. and Clancy M. (1984) The PVT behaviour of gas-condensate systems. *Condensate Reservoir Studies Seminar*, London, October 1984, Paper D, 32 pp., Br. Gas Corp.

Teichmuller M., Teichmuller R. and Bartenstein H. (1979) Inkohlung und Erdgas in Nordwestdeutschland. Eine Inkohlungscarte der Oberflasche des Oberkarbons. *Fortschr. Geol. Rheinl. Westf.* **27**, 137–170.

Thompson K. F. M. (1979) Light hydrocarbons in subsurface sediments. *Geochim. Cosmochim. Acta* **43**, 657–672.

Thompson K. F. M. (1980) Origin of Natural Gas in the San Juan Basin. *26th Int. Geol. Congr.*, Paris, Abstracts, Vol. 2, 789.

Thompson K. F. M. (1983) Classification and thermal history of petroleum based on light hydrocarbons. *Geochim. Cosmochim. Acta* **47**, 303–316.

Thompson K. F. M. (1987) Migration of gas-condensate in deltaic systems. *Mar. Pet. Geol.* Submitted.

Tissot B. P. and Welte D. M. (1984) *Petroleum Formation and Occurrence*, 2nd edn, 538 pp. Springer.

Welte D. H., Kratchovil H., Rullkötter J., Ladwein H. and Schaefer R. G. (1982) Organic geochemistry of crude oils from the Vienna basin and an assessment of their origin. *Chem. Geol.* **35**, 33–68.

Winters J. C. and Williams J. A. (1969) Microbial alteration of crude oil in the reservoir. *Symp. on Petroleum Transformation in Geologic Environments*. Am. Chem. Soc., Pet. Chem. Div. Prepr. **14**, E22–E31.

Yarborough L. (1972) Vapor-liquid equilibrium data for multicomponent mixtures containing hydrocarbon and non-hydrocarbon components. *J. Chem. Eng. Data* **17**, 129–133.

Zhuze T. P. and Yushkevich G. N. (1959) Solubility of oil and its heavy fractions in compressed gases. *Trudy Inst. Nefti Akad. Nauk SSSR* **13**, 262–274.

Zhuze T. P., Ushakova G. S. and Yushkevich G. N. (1962) The influence of high pressures and temperatures on the content and properties of condensate in the gas phase of gas-oil deposits. *Geochemistry* **8**, 797–806.

Zhuze T. P., Yushkevich G. N., Ushakova G. S. and Tumarev K. D. (1963) Use of phase composition data in the system oil-gas at high pressures for ascertaining the genesis of some pools. *Pet. Geol.* **7**, 186–191.